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(54) **Dyed toner**

Farbtoner

Révélateur coloré

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Description

[0001] The present invention relates to a dyed toner for use in copiers, printers, and other image recording devices, and more particularly to a dyed toner comprising fine particles dyed with coloring matter.

[0002] EP-A-0 422 892 discloses a two-component type developer comprising a toner having an electroconductivity lower than 3.5×10^{-10} S/cm.

[0003] JP 61-112160 A discloses a dry process colour toner in which C.I. Solvent Yellow 162(R) is incorporated into a resin, rubber or wax.

[0004] JP 04-241363 A discloses a toner for electrophotography incorporating a methine dye.

[0005] Image recording processes of the prior art employed by printing devices such as copiers, printers, and fax machines can be broadly classified as impact recording processes and non-impact recording processes. Non-impact recording processes include thermal transfer recording, heat sensitive recording, electrophotographic recording, electrostatic recording, ink-jet recording, and other such recording methods. Of these, electrophotographic recording and electrostatic recording employ a toner for developing images on paper or other recording media.

[0006] The basic principle of electrophotographic recording using toner will be described briefly. In this method, the surface of a photosensitive element comprised of a photoconductive substance is first charged to uniform potential. The surface of the photosensitive element is then exposed in response to the image to be output, producing an electrostatic latent image. In the developing section, the resulting latent image is developed by means of toner contained within the developer, producing a visible image. The visible image produced on the photosensitive element surface is transferred to paper or other recording medium, which is transported to a fixing section where it is fixed to the recording medium through heat and pressure.

[0007] The toners employed in the electrophotographic recording process described above comprise fine particles having as their main components a binder resin and coloring matter. The toners can be roughly grouped into a single-component developer comprised of only toner for developing the latent image on the photosensitive element, and a two-component developer comprised of mixtures of toner with glass beads, ferrite, iron powder particles, or the like.

[0008] In the prior art, toners are manufactured by a pulverizing (or milling) process in which the binder and the coloring matter are melted and kneaded together, and then pulverized to the required size using a pulverizer. However, particles pulverized by this method contain large quantities of fine powder, making it necessary to remove the excess fine powder through a classification step in order to produce a uniform particle size distribution.

[0009] The removed fine powder is recovered in the form of unusable particles, so that the yield of final product particles is low relative to the charged amount.

[0010] Methods for manufacturing toner through polymerization, such as suspension polymerization, emulsion polymerization/agglomeration, and dispersion polymerization/dyeing, have been proposed with the goal of solving these problems.

[0011] Suspension polymerization involves combining the coloring matter and the monomer with a poor solvent in which the monomer does not dissolve, dispersing the monomer with a stirring paddle, and then conducting polymerization to produce colored particles.

[0012] This method affords colored particles through a single polymerization process. However, since colored particle size is controlled by the particle size of the monomer dispersed in the solvent, producing small particles (7 μm or smaller) requires conducting polymerization while controlling the heat produced by stirring. However, as there are limits to the vigorousness with which stirring can be conducted, in actual practice it is extremely difficult to produce particle sizes of 7 μm and smaller.

[0013] Particles produced through suspension polymerization also contain large quantities of fine powder, although not in as great amounts as produced in the pulverizing method. Thus, after the colored particles have been dried, a classification step is required.

[0014] The emulsion polymerization/agglomeration method involves combining the monomer and a polymerization initiator with a poor solvent in which the monomer does not dissolve but the initiator does dissolve, and initiating of polymerization the dispersed monomer particles separately produce large quantities of particles about 1 μm in size. A solvent in which these particles, together with the coloring matter, have been dispersed is manipulated so as to cause the 1 μm particles to agglomerate into small particle agglomerates 5 μm or larger in size.

[0015] Particle size distribution of particles manufactured in this way is affected by the stirring conducted during particle agglomeration, so the particle size distribution is similar to that of particles produced through pulverizing processes.

[0016] In the dispersion polymerization/dyeing process, a monomer and a polymerization initiator are simultaneously dissolved in a good solvent in which the monomer will dissolve. As polymerization proceeds, a solvent-insoluble high-molecular weight component settles out, producing particles.

[0017] Particles manufactured using this process have narrow particle size distribution and uniform particle size. However, the coloring matter is incorporated during polymerization, and since it is difficult for coloring to take place

concomitant with polymerization, the particles produced by dispersion polymerization and the coloring matter are re-dispersed in a solvent so that the polymerized particles become dyed with the coloring matter.

[0018] When toners produced using the dispersion polymerization/dyeing process described above (hereinafter referred as "dyed toners") are as recording materials for color printing, yellow, magenta, cyan, and black are required to represent all colors using dyeing toners in four colors. However, in order to represent all colors using four colors, the reproduction range for each color must be wide. If not so, faithful reproduction of all colors will not be possible.

[0019] Dyeing of the polymerized particles is made possible through migration of the dye into the interior of the polymerized particles. However, where the prepared solution for dyeing is of sufficient concentration, the colored particles obtained at the end of the dyed process will in most cases exhibit only minimal migration of the dye. Thus, low dyeing density at completion of the dyeing process is a problem.

[0020] Some dyes have poor lightfastness, while others have poor sublimation, as ascertained by superposing a resin film and examining the color migration.

SUMMARY OF THE INVENTION

[0021] The present invention was developed in order to solve the aforementioned problems, and has as an object to provide a yellow dyed toner having a narrow particle size distribution, excellent lightfastness and sublimation even at small particle size, and high-density color.

[0022] Thus; the present invention provides a dyed toner comprising fine particles of a thermoplastic resin which are dyed with yellow coloring matter, said yellow coloring matter containing at least one methine dye compound; in which:

- (a) the fine particles are produceable by dispersion polymerization;
- (b) the fine particles have a volume average particle diameter of 5-15 μ m;
- (c) the fine particles have a dispersion degree of 1.2 or less;
- (d) the fine particles have a weight average molecular weight of 100,000 or less;
- (e) the fine particles have a cross-linking degree of 50% or less; and
- (f) the fine particles have a flow starting temperature of 200 °C or less when measured by a flow tester under a pressure of 10 kg/cm² and at a heat-up rate of 1°C/min.

[0023] This results in a particle size distribution that is narrow, excellent lightfastness and sublimation, and high yellow density.

[0024] This and other objects, features and advantages of the present invention are described in or will become apparent from the following detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0025] Specific embodiments of the dyed toner of the present invention will now be described.

[0026] The narrow particle size distribution is achieved using dispersion polymerization.

[0027] Dispersion polymerization is also known as precipitation polymerization. A polymerization initiator and a polymer dispersant are simultaneously dissolved in an organic solvent capable of dissolving the monomer, and polymerization is initiated while holding the system at constant temperature. A surfactant or crosslinking agent may be added where necessary.

[0028] An example will be illustrated below for a material using the dispersion polymerization/dyeing method.

(Organic solvent)

[0029] Organic solvents capable of dissolving the polymerizable monomers used in the Working Examples include alcohols such as methanol, ethanol, isopropyl alcohol, n-butanol, s-butanol, t-butanol, n-amyl alcohol, s-amyl alcohol, t-amyl alcohol, isoamyl alcohol, isobutyl alcohol, isopropyl alcohol, 2-ethylbutanol, 2-ethylhexanol, 2-octanol, n-octanol, n-decanol, cyclohexanol, n-hexanol, 2-heptanol, 3-heptanol, 3-pentanol, methylcyclohexanol, 2-methyl-2-butanol, 3-methyl-2-butanol, 3-methyl-1-butyne-3-ol, 4-methyl-2-pentanol, 3-methyl-1-pentyne-3-ol, and mixtures of two or more of the above.

[0030] Examples of organic solvents that can be used concomitantly with these alcohols include hydrocarbon solvents such as hexane, toluene, cyclohexane, benzene and xylene; ethers such as ethylbenzyl ether, dibutyl ether, dipropyl ether, dibenzyl ether, dimethyl ether, tetrahydrofuran, vinyl methyl ether and vinyl ethyl ether; ketones such as acetaldehyde, acetone, acetophenone, diisobutyl ketone, diisopropyl ketone and cyclohexanone; esters such as ethyl formate, ethyl acetate, methyl acetate, ethyl stearate and methyl salicylate; and water. These solvents are used to adjust the alcohol SP value.

[0031] In preferred practice, the organic solvent to monomer weight ratio is 100 : 5 to 80.

(Monomer)

[0032] Compounds containing the vinyl group can be used as polymerizable monomers bearing functional groups. Examples thereof include styrene monomers such as styrene, methylstyrene, ethylstyrene, 2,4-dimethylstyrene, p-n-butylstyrene and p-t-butylstyrene; methyl fatty acid monocarboxylic acid esters such as methyl acrylate, ethyl acrylate, n-butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, 2-ethylhexyl methacrylate, stearyl methacrylate and lauryl methacrylate; vinyl ethers such as methyl vinyl ether, ethyl vinyl ether, n-propyl vinyl ether and n-butyl vinyl ether; vinyl compounds such as acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, ethylene, propylene and chloroprene, used individually or in mixtures of two or more.

(Polymerization initiator)

[0033] In preferred practice the polymerization initiator for polymerizing the aforementioned monomers is added in amounts ranging from 0.001 to 10 wt%. Examples are lauryl peroxide, benzoyl peroxide and azobisisobutyronitrile.

(Dispersant)

[0034] As polymerization proceeds and particles begin to form, a dispersant is added to the organic solvent during the initial stages of polymerization in order to prevent the polymer particles which form from agglomerating. In preferred practice the added amount is 0.1 to 30 weight parts per 100 weight parts of the organic solvent/monomer mixture.

[0035] Examples of dispersants are polystyrene, polyvinyl acetate, polymethyl methacrylate, polydimethylsiloxane, polyvinyl chloride, polyethylene, polypropylene, polylauryl methacrylate, polyoxyethylene, polyvinyl alcohol, polyacrylic acid, polymethacrylic acid, polyacrylamide, polyvinyl pyrrolidone, polyethylene-imine, polyvinyl methyl ether, poly-4-vinyl pyridine, and polystyrenesulfonic acid.

[0036] The monomer and dispersant are suitably mixed into the organic solvent at normal temperature, and a nitrogen purge is conducted. The polymerization initiator is introduced, and the temperature of the dispersed solution is elevated to initiate polymerization. When the temperature reaches 40 to 50°C, the solution begins to turn cloudy, indicating that a solvent-insoluble high-molecular component has begun to precipitate. The polymerization is continued within the range of 50 to 100 °C, provided that the polymerization temperature should be decided in view of a boiling point of the solvent, a decomposition rate of the polymerization initiator and the like.

[0037] Maintaining constant temperature and under stirring, the polymerization reaction is allowed to go to completion over a 5 to 24 hour period while checking the particle size distribution and conversion rate. Once polymerization is complete, the polymer particle dispersion, which up to this point has been held at constant temperature, is allowed to cool to normal temperature, completing the polymerization process series. The polymer particle dispersion is placed in a centrifugal separator to separate the particles from the solution. The product is re-dispersed in solvent to wash away unreacted monomer and dispersant adhering to the particle surfaces. The washing process is conducted over several iterations until it is recognized that no residue remains on particle surfaces, at which point the fine thermoplastic particles are dried.

[0038] Thus, the toner of the invention is one in which the particles have been repeatedly washed with a solvent in order to remove residual colouring matter adhering to the coloured particle surfaces.

[0039] About one hour after the beginning of the polymerization, the formation of the polymer particles can be confirmed, and the particles have a particle average size of 0.1 to 1 µm. Dispersion polymerization is generally continued until a conversion rate of from a monomer to a polymer reaches 90 to 95%, although a conversion rate does not reach 100%. The conversion rate rapidly increases at the initial stage of polymerization, but gradually increases at the last stage thereof. The polymerization is stopped at the time when the particle size reaches the intended size.

[0040] By means of dispersion polymerization, the particle size can be adjusted within the range of 1 to 50 µm. In the present invention the average particle size of a dry toner is 5 to 15 µm.

[0041] In conventional toner manufacture processes such as suspension polymerization or pulverization, toner size can be adjusted within the range of 5 to 15 µm, but a dispersion degree (ratio of a volume-based particle size to a particle-number-based particle size) is 1.3 to 1.5. On the other hand, in dispersion polymerization, particles having a dispersion degree of 1.2 or less can be manufactured.

[0042] The molecular weight of particles obtained according to dispersion polymerization can be adjusted by varying the concentration of an initiator, a dispersing agent or a monomer. The molecular weight distribution can be varied by selecting a chain transfer agent or a monomer to be used. A linking agent can be used upon dispersion polymerization. By adjusting the molecular weight, the molecular weight distribution, thermal properties and shelf stability of the toners can be changed.

[0043] In order to fix the toners on a recording medium by heat and pressure, the particles constituting the toners are required to have a molecular weight of 100,000 or less, a cross-linking degree of 50% or less, an appropriate softening point as a thermoplastics, and a flow-starting temperature of 200°C or less when measured by a flow tester under a pressure of 10kg/cm² and a heat-up rate of 1°C/min.

[0044] The glass transition temperature of the particles affects shelf stability of the toners. If the glass transition temperature is too low, blocking of the toners occurs during storage, and as a result the toners have poor toner-characteristics.

[0045] The glass transition temperature is preferably 50 °C or more in order to have a good shelf stability in the environment. The glass transition temperature can be changed depending on the composition of monomers used, and affects thermal properties of the particles. Accordingly, the glass transition temperature of the particles is preferably about 90 °C or less.

[0046] The fine thermoplastic particles synthesized in the foregoing manner are again dispersed in a solvent for dyeing. The solvent used for dyeing must be one that does not dissolve the fine thermoplastic particles. Examples of the solvent for dyeing include methanol, ethanol, isopropyl alcohol, n-butanol, s-butanol, t-butanol, n-amyl alcohol, s-amyl alcohol, t-amyl alcohol, isoamyl alcohol, isobutyl alcohol, isopropyl alcohol, 2-ethylbutanol, 2-ethylhexanol, 2-octanol, n-octanol, n-decanol, cyclohexanol, n-hexanol, 2-heptanol, 3-heptanol, 3-pentanol, methylcyclohexanol, 2-methyl-2-butanol, 3-methyl-2-butanol, 3-methyl-1-butyn-3-ol, 4-methyl-2-pentanol, 3-methyl-1-pentyn-3-ol, other alcohols, water, and combinations of two or more of the above.

[0047] In preferred practice, the fine thermoplastic particles are used in amounts of 1 to 50 weight parts, more preferably 5 to 30 weight parts and the coloring matter in amounts of 1 to 30 weight parts, more preferably 1 to 10 weight parts per 100 weight parts of the organic solvent.

[0048] Examples of the methine dye compounds that can be used as the coloring matter include Disperse Yellow 31, 49, 61, 73, 82, 87, 88, 89, 90, 91, 93, 99, 116, 118, and 201, Solvent Yellow 32, 79, and 93, and the like. These can be used alone or any combination of two or more thereof.

[0049] In the present invention, dyes other than the methine dye compounds can be used together.

[0050] The solution containing the dispersed fine thermoplastic particles and the coloring matter is heated to 30 to 40°C and held at constant temperature for 30 minutes to two hours under stirring in order to effect dyeing. At completion of the dyeing process, the temperature is lowered to normal temperature and the colored particles and the solvent are separated using a centrifugal separator. The product is repeatedly washed with a solvent and separated in order to remove residual coloring matter adhering to the colored particle surfaces. The mass of colored particles separated from the solvent is dried in a stirred drier held at 30 to 40°C to give fine colored thermoplastic particles.

[0051] The particles are dyed in an organic solvent which should be so selected as not to dissolve the particles. The particles dispersed in the solvent preferably swell therein. The heated, swelling particles adsorb dyes. The higher the heating temperature, the faster the dyeing velocity and the higher the dye concentration in the particles, but this causes the particles to weld together, and the toner constituted of the welded particles loses appropriate functions as a toner. Accordingly the particles are dyed preferably at the glass transition temperature or less of the particles.

[0052] The particles are considered to be dyed in the depth of several μm from the surface thereof. Accordingly, if the particles have a diameter of several μm, they are considered to be dyed up to the central portion thereof, where it is considered that the dye permeates into the inside of the particles, and accordingly that the dye preferably has a chemical structure having a good affinity for the composition of the particles. Of dispersion dyes and oil-soluble dyes, the dye as exemplified above can dye the particles very well.

[0053] Fine particles or release agents can be impinged into the fine dyed thermoplastic particles using a machine such as a hybridizer or mechanofusion in order to fulfill the requirements of durability and fixing properties.

EXAMPLES

[0054] Working Examples of dyed toners will now be described.

Polymer Particle Synthesis Example 1

[0055] In a four-mouthed flask equipped with a stirring paddle, cooler, thermometer, and gas inlet line were mixed 450 weight parts methanol and 150 weight parts isopropyl alcohol. 20 weight parts polyvinyl pyrrolidone (K-30) was dissolved therein. 160 weight parts styrene, 40 weight parts n-butyl acrylate, and 8 weight parts 2,2-azobisisobutyronitrile were added and stirred to give a transparent solution. Under stirring, the atmosphere in the flask was replaced with nitrogen gas, the temperature was elevated to 60°C, and polymerization was initiated under stirring at 100 rpm. 10 minutes after heating the solution began to cloud. Polymerization was allowed to proceed for 10 hours under these conditions.

[0056] 7 hours after the onset of polymerization, 20 weight parts of a 1 : 1 mixture of water and methanol was added

dropwise over a one-hour period while returning the system to normal temperature, terminating polymerization. The resultant slurry was subjected to a first centrifugal separation process using a 3 μm filter. The product was re-dispersed in water/methanol mixed solvent, subjected to a second centrifugal separation process using a 3 μm filter, and then dried overnight. The resultant fine thermoplastic particles had volume-average particle size D_v of 7.2 μm ; the ratio volume-average particle size D_v /number-average particle size D_p (variance) was 1.07.

Polymer Particle Synthesis Example 2

[0057] Particles were prepared using analogous formulation and procedures, excepts that the monomer composition of Polymer Particle Synthesis Example 1 was modified to 160 weight parts styrene and 40 weight parts ethyl acrylate. The resultant fine thermoplastic particles had $D_v = 7.11 \mu\text{m}$ and $D_v/D_p = 1.12$.

Working Example 1

[0058] 100 weight parts methanol was poured into a 300 mL beaker. 3 weight parts C.I. DISPERSE YELLOW 82 was added and dissolved under stirring over a 40°C water bath. 30 weight parts of the dried fine thermoplastic particles prepared in Polymer Particle Synthesis Example 1 was dispersed. Dyeing was conducted for one hour under heating and reflux with stirring. A first centrifugal separation process was conducted using a 3 μm filter, followed by re-dispersion in 100 weight parts of a 1:1 water/methanol mixture. A second centrifugal separation process was conducted. The resultant particles were dried overnight to give yellow dyed particles.

[0059] Hydrophobic silica (RA200H) was mixed with the particles in an amount of 3 weight parts per 100 weight parts particles. The mixture was stirred in mixer to produce a positively charged dyed toner. The charge was measured by combing 4 weight parts dyed toner with 100 weight parts iron powder and measuring with a blow-off charge measurement device; it was found to be +21 $\mu\text{C/g}$.

[0060] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.14) was obtained without offset in the thermal fixing unit, where the reflection density was measured using a Macbeth reflection densitometer RD-917, and was measured through a blue filter. Reflection density of 1.1 or higher is favorable for obtaining yellow images of high density with no irregularities.

Working Example 2

[0061] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 3 weight parts C.I. DISPERSE YELLOW 201 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82.

[0062] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +28 $\mu\text{C/g}$.

[0063] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.22) was obtained without offset in the thermal fixing unit.

Working Example 3

[0064] Yellow died particles were prepared according to the same manner as in Working Example 1, except that the dried fine thermoplastic particles prepared in Polymer Particle Synthesis Example 2 was used in place of those prepared in Polymer Particle Synthesis Example 1, and that the dyeing was conducted for 90 minutes.

[0065] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +24 $\mu\text{C/g}$.

[0066] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.44) was obtained without offset in the thermal fixing unit.

Working Example 4

[0067] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 5 weight parts C.I. DISPERSE YELLOW 31 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82.

[0068] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +33 $\mu\text{C/g}$.

[0069] The dyed toner was packed into a development process having openings, controlling the voltage applied to

electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.23) was obtained without offset in the thermal fixing unit.

Working Example 5

[0070] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 5 weight parts C.I. SOLVENT YELLOW 32 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82.

[0071] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +26 $\mu\text{C/g}$.

[0072] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.31) was obtained without offset in the thermal fixing unit.

Working Example 6

[0073] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 1 weight part C.I. SOLVENT YELLOW 32 and 3 weight parts C.I. DISPERSE YELLOW 201 were used in place of 3 weight parts C.I. DISPERSE YELLOW 82.

[0074] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +38 $\mu\text{C/g}$.

[0075] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.35) was obtained without offset in the thermal fixing unit.

Working Example 7

[0076] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 3 weight parts C.I. DISPERSE YELLOW 201 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82, and that the dried fine thermoplastic particles prepared in Polymer Particle Synthesis Example 2 was used in place of those prepared in Polymer Particle Synthesis Example 1.

[0077] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +26 $\mu\text{C/g}$.

[0078] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.23) was obtained without offset in the thermal fixing unit.

Working Example 8

[0079] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 5 weight parts C.I. SOLVENT YELLOW 32 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82, and that the dried fine thermoplastic particles prepared in Polymer Particle Synthesis Example 2 was used in place of those prepared in Polymer Particle Synthesis Example 1.

[0080] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +24 $\mu\text{C/g}$.

[0081] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.29) was obtained without offset in the thermal fixing unit.

Working Example 9

[0082] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 10 weight parts C.I. DISPERSE YELLOW 201 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82.

[0083] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +20 $\mu\text{C/g}$.

[0084] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.42) was obtained without offset in the thermal fixing unit.

Working Example 10

[0085] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 1 weight part C.I. DISPERSE YELLOW 201 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82, and that 10 weight parts of the dried fine thermoplastic particles were used in place of 30 weight parts thereof.

[0086] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +25 $\mu\text{C/g}$.

[0087] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.24) was obtained without offset in the thermal fixing unit.

Working Example 11

[0088] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 5 weight parts C.I. SOLVENT YELLOW 32 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82, and that the dyeing was conducted in a 50°C water bath.

[0089] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +19 $\mu\text{C/g}$.

[0090] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.45) was obtained without offset in the thermal fixing unit.

Working Example 12

[0091] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 3 weight parts C.I. DISPERSE YELLOW 201 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82, and that the dyeing was conducted in a 50°C water bath.

[0092] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +22 $\mu\text{C/g}$.

[0093] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of sufficient density (reflection density 1.36) was obtained without offset in the thermal fixing unit.

Comparative Example 1

[0094] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 3 weight parts C.I. SOLVENT YELLOW 3 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82.

[0095] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +6 $\mu\text{C/g}$.

[0096] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of insufficient density (reflection density 0.65) was obtained.

Comparative Example 2

[0097] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 5 weight parts C.I. SOLVENT YELLOW 77 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82.

[0098] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +18 $\mu\text{C/g}$.

[0099] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of insufficient density (reflection density 0.23) was obtained.

Comparative Example 3

[0100] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 6 weight parts C.I. SOLVENT YELLOW 7 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82.

[0101] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +12 $\mu\text{C/g}$.

ured in the same manner as in the Working Example 1. The charge value obtained was found to be +27 $\mu\text{C/g}$.

[0102] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of insufficient density (reflection density 0.85) was obtained.

Comparative Example 4

[0103] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 2 weight parts C.I. DISPERSE YELLOW 60 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82, and that 10 weight parts of the dried fine thermoplastic particles were used in place of 30 weight parts thereof.

[0104] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +26 $\mu\text{C/g}$.

[0105] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of insufficient density (reflection density 0.42) was obtained.

Comparative Example 5

[0106] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 5 weight parts C.I. SOLVENT YELLOW 77 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82, and that the dried fine thermoplastic particles prepared in Polymer Particle Synthesis Example 2 was used in place of those prepared in Polymer Particle Synthesis Example 1.

[0107] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +20 $\mu\text{C/g}$.

[0108] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of insufficient density (reflection density 0.29) was obtained.

Comparative Example 6

[0109] Yellow died particles were prepared according to the same manner as in Working Example 1, except that 5 weight parts C.I. SOLVENT YELLOW 77 was used in place of 3 weight parts C.I. DISPERSE YELLOW 82, and that the dyeing was conducted in a 50°C water bath.

[0110] Using the yellow died toner, a positively charged dyed toner was produced and the charge thereof was measured in the same manner as in the Working Example 1. The charge value obtained was found to be +16 $\mu\text{C/g}$.

[0111] The dyed toner was packed into a development process having openings, controlling the voltage applied to electrodes provided to each opening so as to control toner flight, and printing was conducted. A yellow image of insufficient density (reflection density 0.45) was obtained.

[0112] The results as obtained above are tabulated in Table 1, below.

TABLE 1

	C.I. NO.	Reflection density	Charge
Working Example 1	DISPERSE YELLOW 82	1.14	+21 $\mu\text{C/g}$
Working Example 2	DISPERSE YELLOW 201	1.22	+28 $\mu\text{C/g}$
Working Example 3	DISPERSE YELLOW 82	1.44	+24 $\mu\text{C/g}$
Working Example 4	DISPERSE YELLOW 31	1.23	+33 $\mu\text{C/g}$
Working Example 5	SOLVENT YELLOW 32	1.31	+26 $\mu\text{C/g}$
Working Example 6	SOLVENT YELLOW 32 DISPERSE YELLOW 201	1.35	+38 $\mu\text{C/g}$
Working Example 7	DISPERSE YELLOW 201	1.23	+26 $\mu\text{C/g}$
Working Example 8	SOLVENT YELLOW 32	1.29	+24 $\mu\text{C/g}$
Working Example 9	DISPERSE YELLOW 201	1.42	+20 $\mu\text{C/g}$
Working Example 10	DISPERSE YELLOW 201	1.24	+25 $\mu\text{C/g}$

TABLE 1 (continued)

	C.I. NO.	Reflection density	Charge
Working Example 11	SOLVENT YELLOW 32	1.45	+19 $\mu\text{C/g}$
Working Example 12	DISPERSE YELLOW 201	1.36	+22 $\mu\text{C/g}$
Comparative Example 1	SOLVENT YELLOW 3	0.65	+6 $\mu\text{C/g}$
Comparative Example 2	SOLVENT YELLOW 77	0.23	+18 $\mu\text{C/g}$
Comparative Example 3	SOLVENT YELLOW 7	0.85	+27 $\mu\text{C/g}$
Comparative Example 4	DISPERSE YELLOW 60	0.42	+26 $\mu\text{C/g}$
Comparative Example 5	SOLVENT YELLOW 77	0.29	+20 $\mu\text{C/g}$
Comparative Example 6	SOLVENT YELLOW 77	0.45	+16 $\mu\text{C/g}$

[0113] In the dyed toner of the present invention, the fine particles comprised mainly of the thermoplastic resin are dyed with the yellow coloring matter containing at least one methine dye compound, whereby the dyed toner has a narrow particle size distribution, excellent lightfastness and sublimation even at small particle size, and high-density yellow color.

[0114] The entire disclosure of the specification, claims summary and drawings of Japanese Patent Application No. 9-308481 filed on November 11, 1997 is hereby incorporated by reference in its entirety.

Claims

1. An electrophotographic dyed toner comprising fine particles of a thermoplastic resin which are dyed with yellow coloring matter, said yellow coloring matter containing at least one methine dye compound;
in which:
 - (a) the fine particles are producible by dispersion polymerization;
 - (b) the fine particles have a volume average particle diameter of 5-15 μm ;
 - (c) the fine particles have a dispersion degree of 1.2 or less;
 - (d) the fine particles have a weight average molecular weight of 100,000 or less;
 - (e) the fine particles have a cross-linking degree of 50% or less; and
 - (f) the fine particles have a flow-starting temperature of 200°C or less when measured by a flow tester, under a pressure of 10 kg/cm² and at a heat-up rate of 1°C/min.
2. A toner according to claim 1, in which the fine particles have a glass transition point of 50 to 90°C.
3. A toner according to claim 1, in which the methine dye is a Dispersion-type dye.
4. A toner according to claim 2, wherein the weight ratio of thermoplastic resin to yellow coloring matter is from (1 to 50) : (1 to 30).
5. A toner according to claim 3, wherein the yellow coloring matter contains at least one of Disperse Yellow 31, 49, 61, 73, 82, 87, 88, 89, 90, 91, 93, 99, 116, 118 and 201.
6. A toner according to any one of the preceding claims, wherein the particles of thermoplastic resin are dyed by dispersion with the yellow coloring matter in a dyeing solvent.
7. A toner according to any preceding claim, in which the particles have been repeatedly washed with a solvent in order to remove residual colouring matter adhering to the coloured particle surfaces.
8. A toner according to claim 7, in which the solvent is a mixture of methanol and water.
9. A toner according to claim 8, in which the mixture is a 1:1 mixture of methanol and water.

10. An electrophotographic developer composition comprising a dyed toner as defined in any one of claims 1 to 9.

11. Use of a dyed toner as defined in any one of claims 1 to 9 in electrophotographic recording.

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Patentansprüche

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1. Elektrophotographischer Farbtoner mit feinen Partikeln aus einem thermoplastischem Harz, die mit einer gelben färbenden Substanz gefärbt sind, wobei die gelbe färbende Substanz mindestens eine Methinfarbstoffverbindung enthält;

bei dem:

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- (a) die feinen Partikel durch Dispersionspolymerisation herstellbar sind;
- (b) die feinen Partikel einen volumengemittelten Partikeldurchmesser von 5 bis 15 µm aufweisen;
- (c) die feinen Partikel einen Dispersionsgrad von 1,2 oder weniger aufweisen;
- (d) die feinen Partikel ein gewichtsgemitteltes Molekulargewicht von 100.000 oder weniger aufweisen;
- (e) die feinen Partikel einen Vernetzungsgrad von 50% oder weniger aufweisen; und
- (f) die feinen Partikel eine Startfließtemperatur von 200°C oder weniger, wenn mit einem Fließtester gemessen, unter einem Druck von 10 kg/cm² und einer Erwärmungsrate von 1°C/min aufweisen.

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2. Toner nach Anspruch 1, bei dem die feinen Partikel einen Glasübergangspunkt von 50 bis 90°C aufweisen.

3. Toner nach Anspruch 1, bei dem der Methinfarbstoff ein Dispersionsfarbstoff ist.

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4. Toner nach Anspruch 2, bei dem das Gewichtsverhältnis des thermoplastischen Harzes zu der gelben färbenden Substanz von (1 bis 50) : (1 bis 30) beträgt.

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5. Toner nach Anspruch 3, bei dem die gelbe färbende Substanz mindestens eines von Disperse Yellow 31, 49, 61, 73, 82, 87, 88, 89, 90, 91, 93, 99, 116, 118 und 201 enthält.

6. Toner nach einem der vorhergehenden Ansprüche, bei dem die Partikel des thermoplastischen Harzes durch Dispersion mit der gelben färbenden Substanz in einer Farbstofflösung gefärbt sind.

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7. Toner nach einem der vorhergehenden Ansprüche, bei dem die Partikel mit einem Lösungsmittel wiederholt gewaschen sind zum Entfernen verbleibender färbender Substanz, die an den gefärbten Partikeloberflächen anhaftet.

8. Toner nach Anspruch 7, bei dem das Lösungsmittel eine Mischung aus Methanol und Wasser ist.

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9. Toner nach Anspruch 8, bei dem die Mischung eine 1:1-Mischung von Methanol und Wasser ist.

10. Elektrophotographische Entwicklerzusammensetzung mit einem Farbtoner, wie er in einem der Ansprüche 1 bis 9 definiert ist.

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11. Benutzung eines Farbtoners, wie er in einem der Ansprüche 1 bis 9 definiert ist, bei elektrophotographischer Aufzeichnung.

Revendications

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1. Toner électrophotographique teinté comprenant de fines particules d'une résine thermoplastique qui sont teintées par une matière colorante jaune, ladite matière colorante jaune contenant au moins un composé de colorant de méthine,

dans lequel :

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- (a) les fines particules peuvent être produites par polymérisation en dispersion,
- (b) les fines particules présentent un diamètre de particule moyen en volume de 5 à 15 µm,
- (c) les fines particules présentent un degré de dispersion de 1,2 ou moins,

(d) les fines particules présentent une masse moléculaire moyenne en poids de 100 000 ou moins,
(e) les fines particules présentent un degré de réticulation de 50 % ou moins, et
(f) les fines particules présentent une température de début d'écoulement de 200 °C ou moins lorsqu'elle est mesurée par un appareil de mesure d'écoulement, sous une pression de 10 kg/cm² et à une vitesse de montée en température de 1 °C/min.

2. Toner selon la revendication 1, dans lequel les fines particules présentent un point de transition vitreuse de 50 à 90 °C.

3. Toner selon la revendication 1, dans lequel le colorant de méthine est un colorant du type à dispersion.

4. Toner selon la revendication 2, dans lequel le rapport massique de la résine thermoplastique sur la matière colorante jaune est de (1 à 50) : (1 à 30).

5. Toner selon la revendication 3, dans lequel la matière colorante jaune contient au moins l'un des jaunes Disperse Yellow 31, 49, 61, 73, 82, 87, 88, 89, 90, 91, 93, 99, 116, 118 et 201.

6. Toner selon l'une quelconque des revendications précédentes, dans lequel les particules de résine thermoplastique sont teintées par dispersion avec la matière colorante jaune dans un solvant de teinture.

7. Toner selon l'une quelconque des revendications précédentes, dans lequel les particules ont été lavées de façon répétée avec un solvant de manière à éliminer la matière colorante résiduelle adhérent aux surfaces des particules colorées.

8. Toner selon la revendication 7, dans lequel le solvant est un mélange de méthanol et d'eau.

9. Toner selon la revendication 8, dans lequel le mélange est un mélange 1:1 de méthanol et d'eau.

10. Composition de développement électrophotographique comprenant un toner teinté tel que défini dans l'une quelconque des revendications 1 à 9.

11. Utilisation d'un toner teinté tel que défini dans l'une quelconque des revendications 1 à 9 pour un enregistrement électrophotographique.